

†**Electronic Supplementary Information (ESI)**

**Photonic Crystal-based CdS-Au-WO<sub>3</sub> Heterostructure for Efficient Visible-Light Photocatalytic Hydrogen and Oxygen Evolution**

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## Experimental Section

### Chemicals and materials preparation

Methyl methacrylate ( $\geq 99\%$ , Sinopharm Chemical Reagent Co., Ltd.) was refined by reduced pressure distillation to remove the polymerization inhibitor. All other chemicals were used as purchased: Sulfuric acid ( $\text{H}_2\text{SO}_4$ ,  $\geq 98\%$ ), Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ,  $\geq 25\%$ ), Ammonium paratungstate ( $(\text{NH}_4)_6\text{W}_7\text{O}_{24}\cdot 6\text{H}_2\text{O}$ ), Chloroauric acid ( $\text{HAuCl}_4\cdot 4\text{H}_2\text{O}$ , Au content  $\geq 47.8$ ), Polyvinylpyrrolidone (PVP, K-30), Sodium borohydride ( $\text{NaBH}_4$ ,  $\geq 98\%$ ), Cadmium (II) nitrate ( $\text{Cd}(\text{NO}_3)_2$ ,  $\geq 99\%$ ), Thioacetamide ( $\text{C}_2\text{H}_5\text{NS}$ ,  $\geq 99\%$ ), Silver nitrate ( $\text{AgNO}_3$ ,  $\geq 99\%$ ), Sodium sulfite ( $\text{Na}_2\text{SO}_3$ ,  $\geq 97\%$ ) and Sodium sulfide ( $\text{Na}_2\text{S}$ ,  $\geq 98\%$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd.

*Synthesis of Colloidal Crystal Templates:* Monodispersed poly(methyl methacrylate) (PMMA) microspheres latex were prepared via batch emulsion polymerization according to the procedure our group reported previously.<sup>[S1]</sup> The PMMA latex was centrifuged and redispersed into deionized water and ethanol mixed solution (1:1 volume ratio) to form a colloidal suspension with PMMA content of 20 wt%. The colloidal crystal films were prepared via a modified vertical deposition method on quartz glass slides.<sup>[S2]</sup> Typically, the quartz glass slides ( $2 \times 5$  cm) were soaked in the mixed  $\text{H}_2\text{SO}_4$  (98%) and  $\text{H}_2\text{O}_2$  (25%) solution with the volume ratio of 3:1 for 3 h, and then they were washed with deionized water to make the surface hydrophilic. Subsequently, the hydrophilic glass slides were vertically submerged onto the prepared PMMA colloidal suspension with diameter 180, 240 and 310 nm for 1 min, then pulled out and horizontally positioned in a closed culture dish for drying at room temperature. Before using, the colloidal crystal films were annealed at 100 °C for 30 min.

*Synthesis of  $\text{WO}_3$  Inverse Opal Photonic Crystals:*  $\text{WO}_3$  inverse opal PCs were prepared using  $(\text{NH}_4)_6\text{W}_7\text{O}_{24}\cdot 6\text{H}_2\text{O}$  solution ( $\text{H}_2\text{O}$  and methanol 7: 3 volume ratio) as the precursor. To avoid redundant precursor staying on the surface of colloidal crystal template to affect the quality of inverse opal PC, a filter paper was immersed in the precursor solution, and then covered it to the template film. After drying at room

temperature, the samples were heated to 500 °C at a rate of 1°C·min<sup>-1</sup> and held for 2 h. Crushed WO<sub>3</sub> was prepared via crushing mixed PC segments of WO<sub>3</sub>-180, WO<sub>3</sub>-240 and WO<sub>3</sub>-310.

*Deposition of Au Nanoparticles:* For effective control of the dispersion and size of supported Au nanoparticles, gas-bubbling-assisted membrane reduction method was employed.<sup>[S1]</sup> 100 mL deionized water, 1.5 mL stabilizer of PVP (0.1 M), 1.25 mL HAuCl<sub>4</sub> (5 g/L) solution, and 0.1 g of WO<sub>3</sub> PC segments scrapped from the glass substrate were added to a beaker. The solution mixture was driven by a peristaltic pump at flow rate of 220 mL·min<sup>-1</sup> to form a tubal cycling flow. Reductant of 50 mL NaBH<sub>4</sub> (0.04 M) solution was slowly injected (1 mL·min<sup>-1</sup>) by plunger pump through the channels (d=40 nm) of ceramic membrane into tubular reactor. After the NaBH<sub>4</sub> solution was added completely, the reaction system was further kept peristalsis and stirred for 30 min. Then, the product was filtered and washed with ethanol and deionized water to remove the PVP and Cl<sup>-</sup> sufficiently. The final sample was dried at 60 °C and the desired Au-WO<sub>3</sub> was obtained. Au nanoparticles were prepared by the same process but without WO<sub>3</sub> support.

*Coating of CdS Shell:* Hydrothermal coprecipitation method was used to coat CdS on Au nanoparticles. The 0.1 g as-prepared Au-WO<sub>3</sub> was added to a 15 mL aqueous solution containing 0.03 mmol C<sub>2</sub>H<sub>5</sub>NS and stirred continuously for 12 h. Then 0.3 mmol Cd(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was added and further stirred for 30 min. The solution was transferred into a teflon-lined stainless-steel autoclave (23 mL capacity) and elevated temperature (1°C·min<sup>-1</sup>) to 120 °C and hydrothermally treated for 12 h. The sample was then collected and washed by deionized water three times. Reference samples of CdS-WO<sub>3</sub>, CdS-Au and CdS were prepared through the same method except for the addition of WO<sub>3</sub>, Au and nothing instead of Au-WO<sub>3</sub>, respectively.

## **Characterization**

Powder X-ray diffraction (XRD) patterns were recorded with a diffractometer (Shimadzu XRD 6000) using Cu K $\alpha$  ( $\lambda = 0.15406$  nm) radiation with a Nickel filter operating at 40 kV and 10 mA in the 2 $\theta$  range of 10-90° at a scanning rate of 4°·min<sup>-1</sup>.

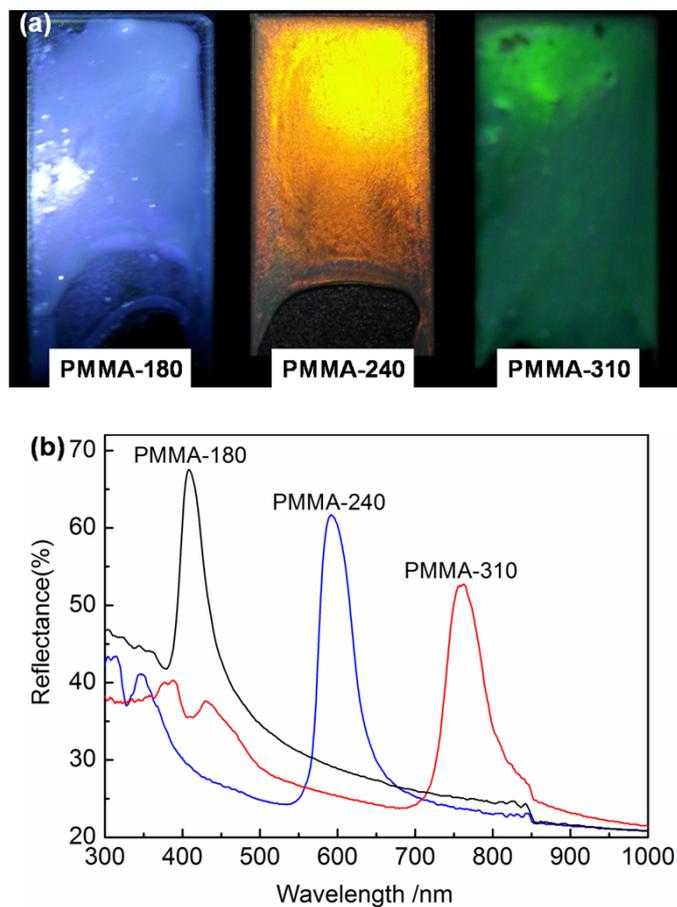
<sup>1</sup>. The patterns were compared with JCPDS reference data for phase identification. The UV-Vis diffused reflectance spectra (DRS) experiments were performed on a UV-Vis spectrophotometer (Hitachi U-4100) with the integration sphere diffuse reflectance attachment. The Brunauer–Emmett–Teller (BET) surface areas were measured by N<sub>2</sub> adsorption and desorption using a Micromeritics ASAP2010 analyzer. The surface morphology of the samples was observed by Scanning electron microscopy (SEM) of FEI Quanta 200F at an accelerating voltage of 30 kV. Images of transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were obtained with a JEOL JEM-2100 electron microscope equipped with a field emission source at an accelerating voltage of 120 kV. Samples for TEM were prepared by sonicating small amounts of the powder in 5 mL of ethanol for 5 min and then deposited a few drops of the suspension on a holey carbon grid. The size of particles was measured from TEM images and the average particle diameter was calculated from the mean diameter frequency distribution with the formula:  $d = \sum n_i d_i / \sum n_i$ , where  $n_i$  is the number of particles with a particle diameter  $d_i$  in a certain range. Image of scanning transmission electron microscopy (STEM) and Energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were obtained with an FEI F20 field emission source electron microscope operating at 200 kV accelerating voltage equipped with a LaB6 electron gun and the procedure of preparing samples were same to the TEM.

### **Photocatalytic reaction**

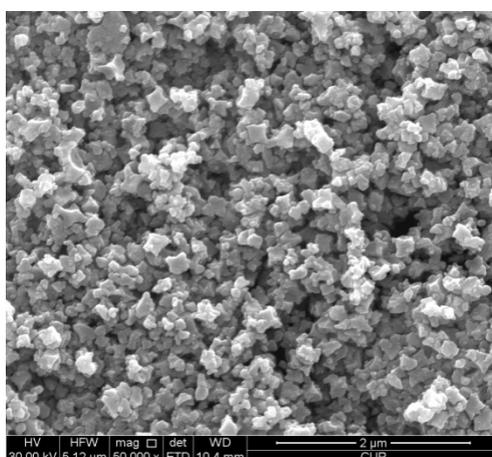
The hydrogen production was performed in LabSolar-H2 system under visible light irradiation in an aqueous solution (100 mL) containing 20 mg photocatalysts, Na<sub>2</sub>S (20 mmol), and Na<sub>2</sub>SO<sub>3</sub> (20 mmol). A 300 W Xe arc lamp was used as a light source. Light passed through a 3.5 cm IR water filter and an UVcutoff filter ( $\lambda > 420$  nm), and then the filtered light was focused onto the reactor. Prior to light illumination used, the reaction setup was vacuumed and it should be air-free. During irradiation, the headspace gas (ca. 4.23 mL) of the reactor was intermittently sampled every 30 minutes and the H<sub>2</sub> and O<sub>2</sub> from the headspace gas were analyzed by a gas

chromatograph (BEIFEN, China) equipped with a thermal conductivity detector and a 5 Å molecular sieve column and Ar as carrier gas.

## Results Section

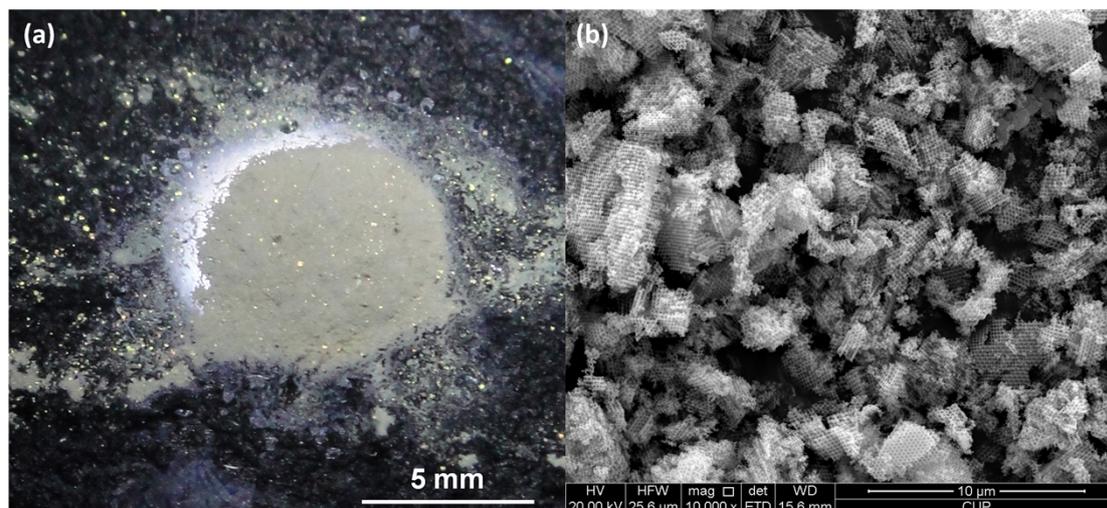


**Fig. S1** Optical images (a) and reflectance spectra (b) of different diameter (180, 240 and 310 nm) PMMA photonic crystal films with photonic stop-band maxima at 408, 592, and 760 nm.

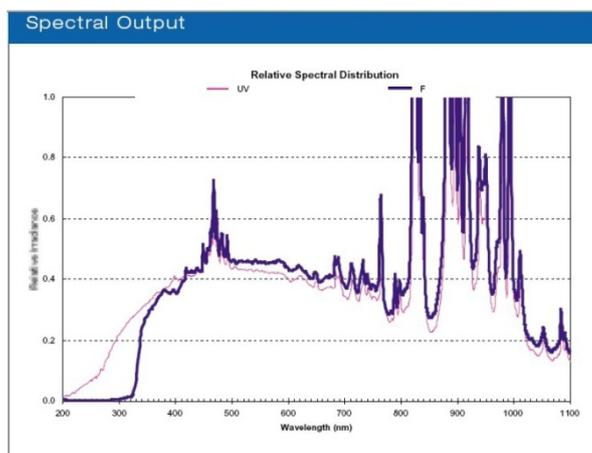


**Fig. S2** SEM image of crushed  $\text{WO}_3$  obtained from crushing mixed PC segments of

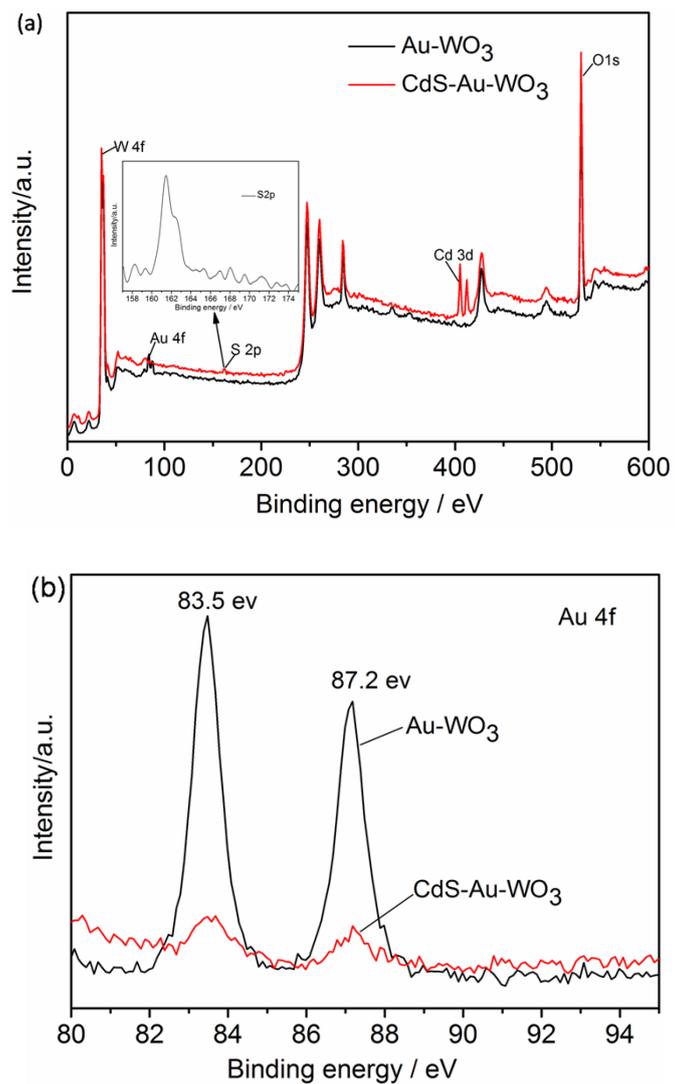
WO<sub>3</sub>-180, WO<sub>3</sub>-240 and WO<sub>3</sub>-310.



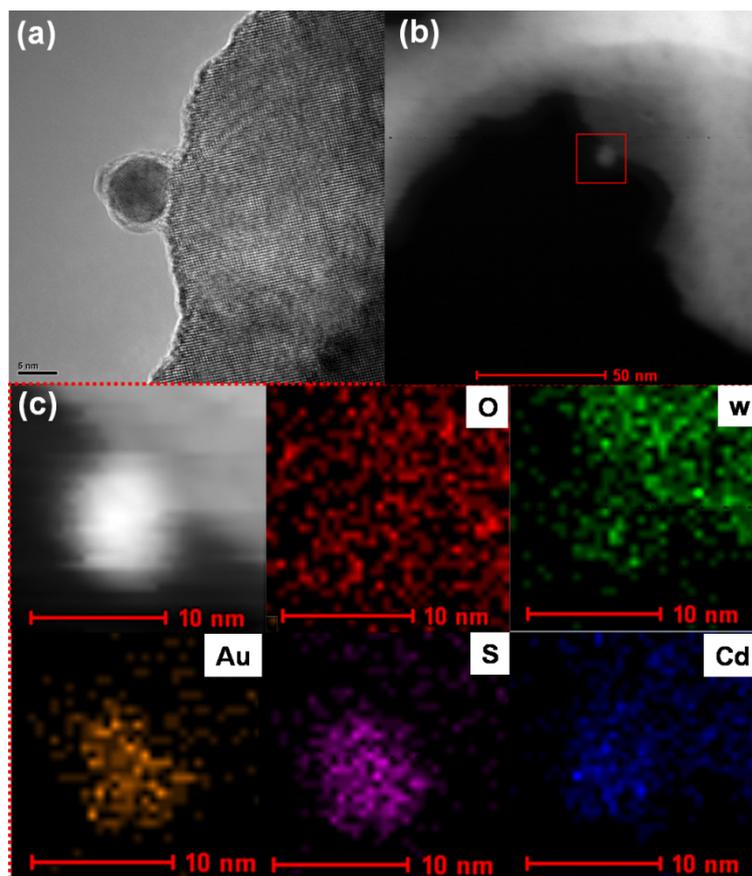
**Fig. S3** Optical (a) and SEM (b) images of WO<sub>3</sub>-240 PC segments exfoliated from the glass substrate. The optical image shows bright structure colors and the SEM image displays that the segments are keep highly ordered macrospores structure in some range.



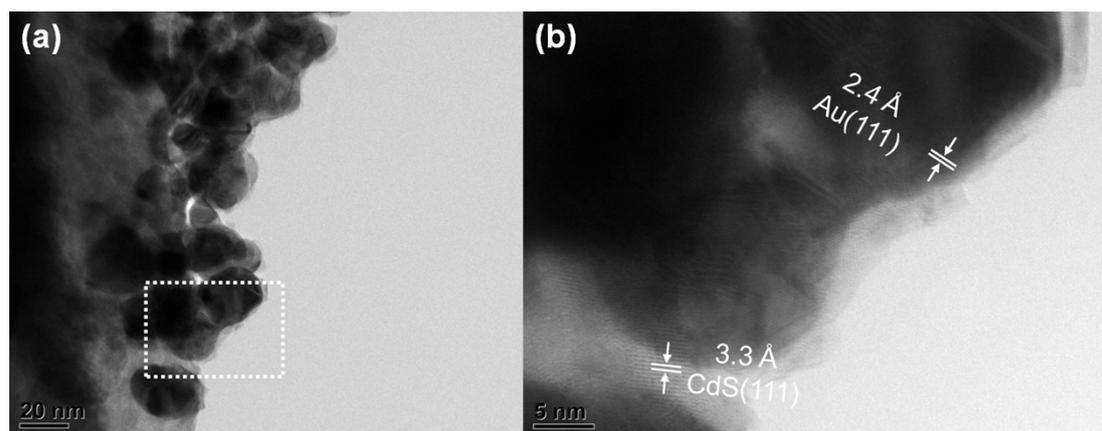
**Fig. S4** The emission spectrum (dark blue one) of the Xe lamp employed in the hydrogen evolution measurement.



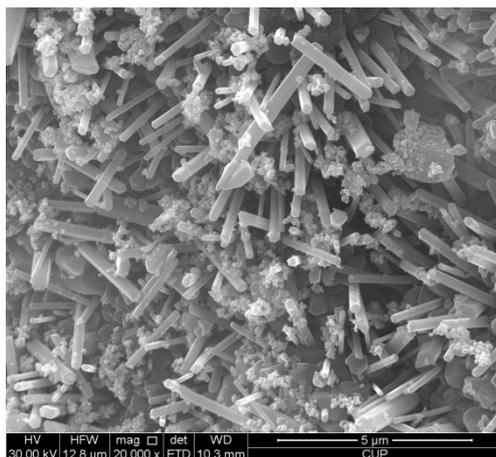
**Fig. S5** XPS survey spectra (a) and high resolution spectra for Au 4f (b) of Au-WO<sub>3</sub> and CdS-Au-WO<sub>3</sub>.



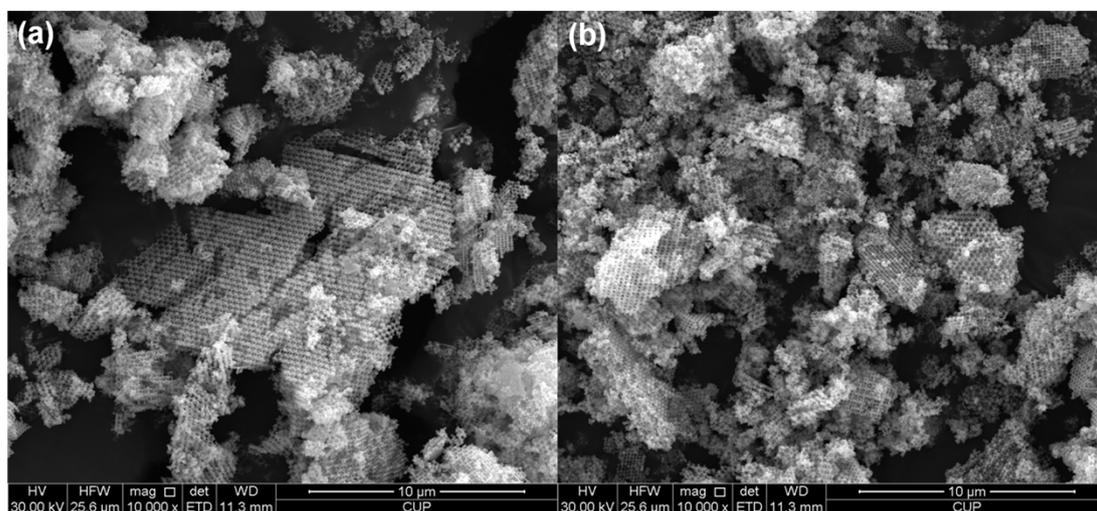
**Fig. S6** HRTEM image (a), corresponding STEM image (b), EDS elemental mapping images (c) of CdS-Au-WO<sub>3</sub>.



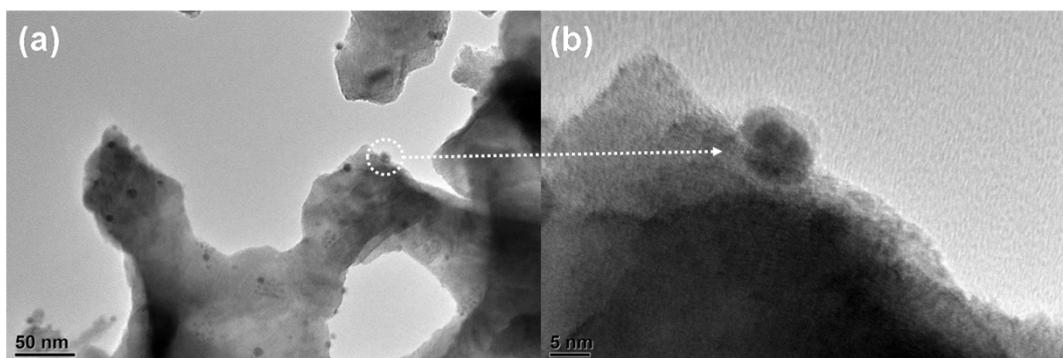
**Fig. S7** TEM (a) and HRTEM (b) images of CdS-Au core shell particles



**Fig. S8** SEM image of CdS prepared by hydrothermal coprecipitation.

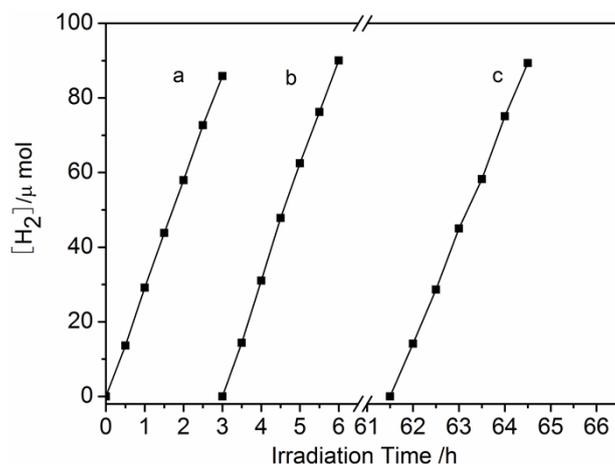


**Fig. S9** SEM images of WO<sub>3</sub>-240 PC segments after stirring 72 h in the aqueous solution (a) and the CdS-Au-WO<sub>3</sub> after photocatalytic H<sub>2</sub> evolution reaction for 12 h (b).

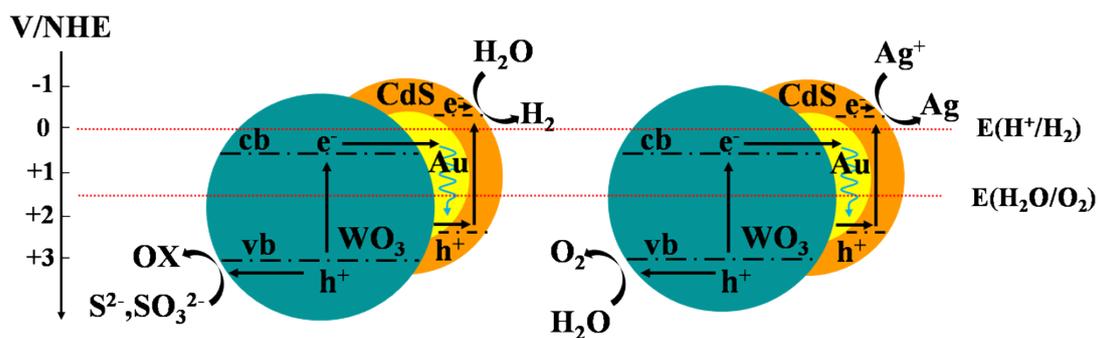


**Fig. S10** TEM (a) and HRTEM (b) images of CdS-Au-WO<sub>3</sub> after continuous reaction

12 h for H<sub>2</sub> evolution



**Fig. S11** Hydrogen evolution profiles of CdS-Au-WO<sub>3</sub> under visible-light illumination over 100 mL aqueous solution contain 20 mg photocatalyst and 20 mmol Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as sacrificial reagents; 300 W Xe arc lamp with a UV-cutoff filter ( $\geq 420$  nm) used as the visible-light source. (a) Reaction for 3 h; (b) evacuate and continue reaction for another 3 h; (c) illuminate for 55.5 h, evacuate system, and continue reaction for 3 h.



**Scheme S1.** Schematic of the vectorial charge carrier transfer process in the CdS-Au-WO<sub>3</sub> heterostructure.

**Table S1.** BET surface area of the WO<sub>3</sub>-180, WO<sub>3</sub>-240, and WO<sub>3</sub>-310 photonic crystal segments and WO<sub>3</sub>-cru.

Samples	WO <sub>3</sub> -180	WO <sub>3</sub> -240	WO <sub>3</sub> -310	WO <sub>3</sub> -cru
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BET (m <sup>2</sup> /g)	13.3	12.3	10.3	12.8
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### References

- [S1] Y. C. Wei, J. Liu, Z. Zhao, Y. S. Chen, C. M. Xu, A. J. Duan, G. Y. Jiang, H. He, *Angew. Chem. Int. Ed.* 2011, **50**, 2326.
- [S2] P. Jiang , K. S. Hwang , D. M. Mittleman , J. F. Bertone , and V. L. Colvin, *J. Am. Chem. Soc.*, 1999, **121** ,11630.